

Name:
Section: (Peter, Janette, Richard, Stephen)

SID:

FINAL EXAM
Biophysical Chemistry
Chemistry 130A
Spring 2001

Justify all your assumptions!

Show all your calculations!

Make sure all your conclusions are physically reasonable.

Keep track of units and significant digits!

Underline or Box all your final answers!

Exams in pencil won't be regraded.

Keep your answers short!

Problem	Points
1	
2	
3	
4	
5	
6	
7	
8	
Total	

Name:
Section: (Peter, Janette, Richard, Stephen)

SID:

Physical Constants

Gas Constant	R = 8.3145 J/K mol = 0.08205 L atm/K mol	Boltzmann constant	k = 1.381*10 ⁻²³ J/K
RT @ 25°C	RT = 2.479 kJ/mol = 24.464 L atm/mol	kT @ 25°C	kT = 4.116*10 ⁻²¹ J
Faraday constant	F = 9.648*10 ⁴ C/mol	K _f for H ₂ O @ 1 atm	K _f = 1.86 K kg solvent/moles solute
	1 atm = 1.01325 * 10 ⁵ Pa = 760 Torr = 760 mm Hg		

Physical Equations

Raoult's Law	$P_A = X_A P_A^\circ$	Henry's Law	$P_B = \kappa_B X_B$
van't Hoff Eq.	$\ln \frac{K_2}{K_1} = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$	Osmotic Pressure	$\ln(a_A) = \frac{-\pi \bar{V}_A}{RT}$
Freezing/Boiling Changes	$ \Delta T_{f,b} = K_{f,b} m_B$	Osmotic Pressure	$\pi = cRT$
Freezing/Boiling Changes	$ \Delta T_{f,b} = \frac{M_A R T_o^2}{1000 \Delta H_{fus,vap}} m_B$	Free Energy	$\Delta G = \Delta G^\circ + RT \ln(Q)$
Chemical Potential	$\mu = \mu^\circ + RT \ln(a)$	Free Energy	$dG = VdP - SdT + \mu dn + \gamma dA + ZF d\phi + Mgdh - M\omega^2 dx$
Total Energy	$\Delta E = q + w$	Enthalpy	$\Delta H = \Delta E + \Delta(PV)$
Heat Capacity	$q = \int_{T_1}^{T_2} C(T) dT$	Entropy	$dS = \frac{dq_{rev}}{T}$
Average Translational Energy	$\langle U_{tr} \rangle = \frac{3}{2} kT$	Mean Speed	$\langle u \rangle = \left(\frac{8kT}{\pi m} \right)^{1/2}$
Maxwell Distribution	$P(u) = 4\pi \left(\frac{m}{2\pi kT} \right)^{3/2} u^2 e^{-mu^2/2kT}$	Mean Square Speed	$\langle u^2 \rangle = \frac{3kT}{m}$
Boltzmann Distribution	$\frac{P_j}{P_i} = \frac{N_j}{N_i} = \frac{g_j}{g_i} e^{-(E_j - E_i)/kT}$	collisions per second per molecule	$z = \sqrt{2\pi} \frac{N}{V} \sigma^2 \langle u \rangle$
Mean Free Path	$\lambda = \frac{\langle u \rangle}{z}$	collisions per unit volume per unit time	$Z = \left(\frac{N}{V} \right) \frac{z}{2}$
Scatchard Equation	$\frac{v/N}{[A]} = K(1 - v/N)$	Hill Equation	$\frac{f}{1-f} = K[A]^n$
Fick's 1 st Law	$J_x = -D \frac{dc}{dx}$	Michaelis-Menten Law	$v = k_{cat} E_{tot} \frac{[S]}{K_M + [S]}$
Pressure	$P = \rho gh$		$V_{max} = k_{cat} E_{tot}$
Arrhenius' Law	$k = A \exp\left(\frac{-E_a}{RT}\right)$	Diffusion Constant	$D = \langle x^2 \rangle / 2t$
Nernst Equation	$\mathcal{E} = \mathcal{E}^0 - \frac{RT}{nF} \ln(Q)$	Transition State Theory	$k = \frac{k_B T}{h} \exp\left(\frac{\Delta S^\ddagger}{R}\right) \exp\left(\frac{-\Delta H^\ddagger}{RT}\right)$

Name:

SID:

Section: (Peter, Janette, Richard, Stephen)

You have received a tissue sample from an animal captured near the mouth of an active volcano drinking salty run-off from a hot stream that runs by the magma flow. You are interested in the mechanisms by which the animal cells deal with the raised salt and temperature conditions.

1. In order to determine the osmotic properties of the cells, you put them in a 0.25 M sucrose solution at 25 °C

a) Under a microscope, you observe that the cells swelling to about 120% their original volume. Assuming the cell membrane provides no resistance to the swelling and that the inside of the cell is just simple inorganic salt solution and the membrane is permeable only to water, what was the initial concentration of salt inside the cell?

b) What would the pressure causing the cells to expand have been just after addition of the sucrose solution?

Name:

SID:

Section: (Peter, Janette, Richard, Stephen)

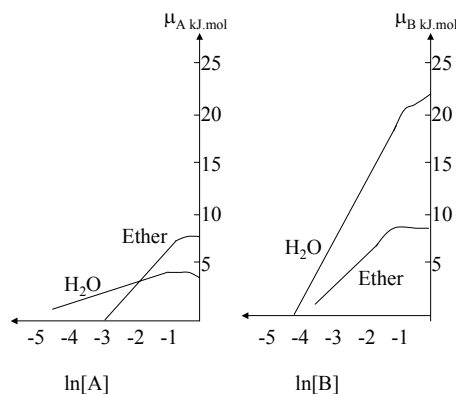
c) Despite the simplifying assumption in (a), real cells attempt to maintain their internal salt concentration using ion pumps that work against the concentration gradients by hydrolyzing ATP. Cells leak salt slowly and so these pumps work even in the absence of osmotic stress. If the normal KCL concentration outside the cell is 1mM, and the inside is 100mM, what fraction of the free energy available from the hydrolysis of one mole of ATP (-25kJ at 25 °C) is used to transport one mole of KCL to the cell's exterior.

Name:

SID:

Section: (Peter, Janette, Richard, Stephen)

2. When you break open the cells that come into closest contact with the hot stream of water from problem 1 you find two particular proteins in abundance. You decide to isolate these proteins, A and B, for further study. You find that these proteins, despite their high concentrations, are only partially soluble in water. Curious about the solubility properties of these proteins you measure their chemical potential (at 25 °C) as a function of concentration in water and in an organic standard, diethyl-ether.



a) What are the standard state chemical potentials of A and B in each solvent?

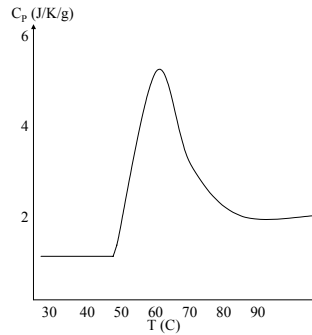
b) If A is dissolved in water at low concentration and then diethylether is brought into contact (the ether is not miscible in water), find the ratio $[A]_{\text{water}}/[A]_{\text{ether}}$ when the system comes to equilibrium.

Name:

SID:

Section: (Peter, Janette, Richard, Stephen)

3. You decide to further study protein A for its thermostability. You discover this protein is monomeric (one subunit) and weighs about 14 kD. You decide to study it with differential scanning calorimetry. The machine produces a heat capacity as, C_p , as a function of temperature. You get the curve below:



a) Using these data estimate the “melting” temperature, T_m , for this protein.

b) Estimate ΔC_p for the folded to unfolded transition.

c) Estimate the values for $\Delta H(T_m)$ and $\Delta S(T_m)$ for this protein.

d) Set up all the equations you need to solve for the ratio of unfolded protein concentration to folded protein concentration at 30 °C. Show a thermodynamic path diagram to backup your equations. You do not need to solve them.

Name:

SID:

Section: (Peter, Janette, Richard, Stephen)

4. While doing a routine spectroscopic analysis of your cellular sample you note that there is a high concentration of mercury. Further, you find that this normally poisonous metal is also found in your purified protein A preparation. You hypothesize that your protein binds one Hg^{2+} ion and you decide to measure the binding constant electrochemically at 25 °C.

a) First you set out to measure the standard electrochemical potential of your anode. Your electrochemical cell has a standard hydrogen electrode on one side and in the other a mercury (Hg metal) electrode in a 50 μM Hg^{2+} solution. The cell voltage for the reaction $\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg (metal)}$ was determined to be 1.582 volts. What is the standard electrochemical potential for the $\text{Hg}^{2+} + 2\text{e}^- \rightarrow \text{Hg (metal)}$ half-cell?

b) You then add protein A to the mercury side of the electrochemical cell above to make a protein concentration of 100 μM . The measured cell voltage is then 1.444 V. What is the equilibrium constant for binding of Hg^{2+} to A? Assume that the mercuric ion/protein complex is electrochemically inactive!

SID:

5. Suppose that when a particular channel in the sarcoplasmic reticulum (SR) in a cell is activated it allows calcium ion to flow across the SR membrane. In fact, it is found that this particular channel transports four ions at a time into the cell cytoplasm. In this particular cell the potential of the cytoplasmic side is 100 mV less than inside the SR. Consider the system at 37 °C. It is measured that there is a Ca^{2+} concentration of 20.0 μM inside the SR and a concentration of 1.00 μM Ca^{2+} in the cytoplasm.

i. In the absence of active transport, what is the value of the free energy per mole for the transport of calcium from the SR to the cytoplasm of the cell? In which direction will the calcium ion spontaneously flow through the membrane channel?

ii. Determine the minimum amount of ATP which would need to be hydrolyzed in order to reverse the spontaneous direction of the calcium flux found in part i, given that ΔG° for the hydrolysis of ATP is -31.3 kJ/mol and that the reaction quotient, Q, for the hydrolysis is about 10^{-2}

Name:
Section: (Peter, Janette, Richard, Stephen)

SID:

- (b) Assume that a single channel in the SR is activated and in a very short space of time has transported a small amount of calcium from the SR to the cytoplasm and then has closed. This leaves a small point source of calcium ion just at the SR membrane. The tiny sphere contains $w_0 = 40$ nanograms of Ca^{2+} . The diffusion constant for calcium ion in cytoplasm is $64 \times 10^{-6} \text{ cm}^2/\text{sec}$. The number of grams per ml of calcium ion at a distance r away from the sphere at any time t is:

$$c(r,t) = \frac{w_0}{(4\pi Dt)^{3/2}} \exp\left(-\frac{r^2}{4Dt}\right)$$

Suppose there is a receptor 20 micrometers (microns) away from the tiny sphere. It requires at least $8 \mu\text{g}/\text{cm}^3$ of ion locally around the receptor in order to be activated. Will it be activated at $t=10$ milliseconds after the channel opening? Ignore any blocking of calcium diffusion by cellular structures. Show your calculations.

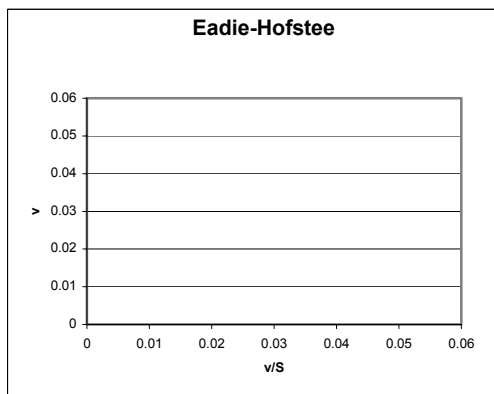
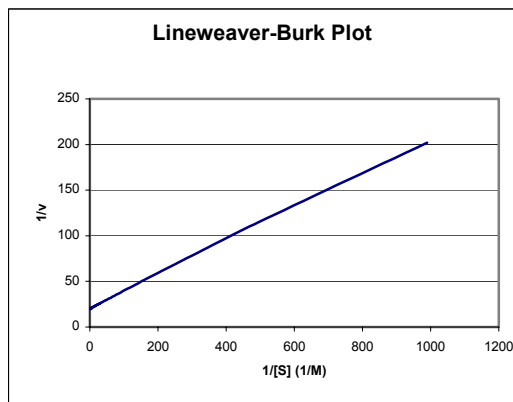
- (c) In real cells there are hundreds of proteins in the cytoplasm that bind calcium ions. What would you expect, qualitatively, the effect of these proteins would be on
- the apparent diffusion constant for Ca^{2+} and
 - its peak concentration at any point in time?

Name:

SID:

Section: (Peter, Janette, Richard, Stephen)

6. As it turns out your protein, now called E, catalyzes the production of a substance P from a substance S. (What a coincidence!) The Lineweaver-Burk plot for this enzyme (at 10 °C) is given in the figure below.



a) What are K_m and V_{max} for this experiment? Draw how the same curve would look on an Eadie-Hofstee plot on the empty graph above (label the slope and intercept with values). (If you don't know what an E-H plot is, derive it from the Michaelis-Menten equation and the labels on the axes.)

b) When the temperature of the same reaction mixture is increased to 25 °C the value of V_{max} increased 2.9 times. Calculate the activation energy for the reaction. According to the Michaelis-Menten kinetics model, to which elementary step in the overall reaction does this activation energy correspond to? Write down the elementary steps.

Name:

SID:

Section: (Peter, Janette, Richard, Stephen)

c) When you add mercuric ion to the solution and repeat the experiment you find that the initial rate of production of product at all substrate concentration is increased. Propose a modification to the basic reaction mechanism below if this effect is due to binding of the mercuric ion to a site other than the active site on the enzyme.



d) For the modified reaction mechanism above, set up the equations (as guided below), that are necessary to solve for the rate of production of P in terms of only : total enzyme, mercuric ion concentration, substrate concentration and kinetic and thermodynamic constants.

differential relations

conservation relations

thermodynamic relations

state the assumptions that are necessary for the above equations to be written.

Name:

SID:

Section: (Peter, Janette, Richard, Stephen)

e) How would you expect the addition of activator to change the Lineweaver-Burk plot above (slope, intercepts.) Explain why from the mechanism and equations proposed.

Name:

SID:

Section: (Peter, Janette, Richard, Stephen)

7. All radioactive decay follows first order kinetics, that is, the amount that decays is dependent only upon the mass of material present. There are many examples of decay chains where the starting material (called the parent) decays to another material (called the daughter) that is itself radioactive; further, the grand-daughter may also be radioactive, and so on. Each of these substances has a particular decay rate constant.

^{135}I decays to ^{135}Xe by β^- emission with a characteristic half-life of 6.6 hours

^{135}Xe decays to ^{135}Cs by β^- emission with a characteristic half life of 9.1 hours.

For our purposes, assume ^{135}Cs is stable.

Write down the equations that determine the amount of each isotope present with respect to time. You don't have to solve them.

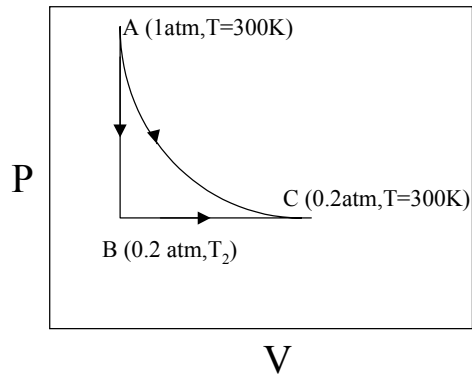
b) Calculate the decay rate constants for each ^{135}I and ^{135}Xe . About how many half-lives does it take to get down to 0.1% of our isotopes?

c) Draw a reasonably quantitative graph for the amounts of each isotope as a function of time starting with some amount, N_0 , of ^{135}I .

Name:
Section: (Peter, Janette, Richard, Stephen)

SID:

8. This question concerns the following processes for 1 mole of an ideal gas:



Where Path I goes $A \rightarrow B \rightarrow C$ and Path II goes from $A \rightarrow C$ and

Process $A \rightarrow B$ is constant volume, irreversible depressurization.

Process $B \rightarrow C$ is constant pressure, irreversible expansion.

Process $A \rightarrow C$ is an isothermal, reversible expansion

a) Calculate the difference in work following Path I versus Path II for 1 mole of an ideal gas.

b) Calculate ΔS for Path I. Calculate ΔS for path II.

c) Qualitatively, compare the $A \rightarrow C \rightarrow B \rightarrow A$ cycle to the efficiency of a Carnot engine. Is it greater than, less than, or equal to that efficiency? Why?